A Hybrid Carbon Capture System of Indirect Calcination and Amine Absorption for a Cement Plant

Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 63 (2014) 6428 – 6439

Energy Procedia

GHGT-12

A Hybrid Carbon Capture System of Indirect Calcination and Amine Absorption for a Cement Plant

Dursun Can Ozcan, Stefano Brandani, Hyungwoong Ahn*

Scottish Carbon Capture and Storage (SCCS), Institute for Materials and Processes, School of Engineering, The University of Edinburgh

Abstract

Here we present the process integration of the indirect calcination process existing in the literature [1] into a cement plant. The indirect calcination process is composed of a circulating fluidized bed combustor and a fluidized bed calciner where hot solid particles are circulated between those reactors for heat transfer. It allows separation of CO_2 from limestone calcination in a concentrated form. The process integration proposed in this study minimizes the total thermal energy requirement by using excess energy from high temperature flue gases for cement raw meal preheating as in the conventional cement manufacturing process. It also suggests a new hybrid carbon capture system where an additional CO_2 capture unit is combined with the indirect calcination process, since the standalone indirect calcination application can only provide a moderate level of CO_2 avoidance. The amine process is added to increase CO_2 avoidance rate further. Full process flowsheets have been developed and analyzed using the commercial software UniSim Design R400 from Honeywell. The hybrid system can achieve more than 90% carbon capture rate thanks to the supplementary amine process while the indirect calcination can capture only 56% without the amine process. With the support of a simple and transparent economic analysis, the capture cost involved in the hybrid system was estimated to be higher than that of the indirect calcination only but significantly lower than that of the standalone amine process on a basis of unit CO_2 avoided.

Peer-review under responsibility of the Organizing Committee of GHGT-12

Keywords: carbon capture; indirect calcination; amine process; cement plant.

* Corresponding author. Tel.: +44-131-650-5891; fax: +44-131-650-6551.
E-mail address: h.ahn@ed.ac.uk

Peer-review under responsibility of the Organizing Committee of GHGT-12
doi:10.1016/j.egypro.2014.11.678

1. Introduction

Long-term climate change is associated with increasing concentration of CO_2 as a major greenhouse gas in the atmosphere [2]. According to Intergovernmental Panel on Climate Change, consequential reductions of global CO_2 emissions by at least 50% are necessary by 2050 [3]. Even though more elaborate studies have been under investigation for the power sector, cement industry is responsible for remarkable CO_2 emissions amounting over 2 billion tons of CO_2 per year [4, 5]. Therefore, it is important to extend the limit of the carbon capture studies including cement industry in order to achieve the CO_2 capture target projected over the next 40 years.

So far, there have been many separation processes studied for carbon capture from cement plants, such as amine process, calcium looping (Ca-looping) process, indirect calcination, etc. The amine process is the most conventional and commercially available process, which is capable of achieving very high CO_2 purity and recovery at the same time. When applied to a cement plant the amine process is likely to have very high energy penalty per recovered CO_2 compared to an amine process in a coal-fired power plant. This is because a combined heat and power (CHP) plant for steam generation for the stripper reboiler and power would not be designed as efficiently as a steam cycle of a coal-fired power plant.

As an alternative to the amine process, Ca-looping processes have been studied in detail. The energy penalty of a Ca-looping process including CO_2 compression integrated with a cement plant has been estimated to be at minimum 2.5 GJ_{th}/ton CO_2 avoided [6]. In particular, Ca-looping processes would be more efficient when applied to cement plants rather than power plants since the purge stream from a Ca-looping cycle can be fed to a cement kiln resulting in improving the clinker production rate. However, the estimated reduction of energy penalty is only possible when a steam cycle is deployed to recover the process heat and generate power. The construction cost involved in deploying the heat recovery steam cycle can be significant relative to that for Ca-looping unit.

Indirect calcination must be the simplest configuration among all of them since it does not require oxygen and involves a very low energy penalty. However, there is a maximum carbon capture rate that can be achieved with indirect calcination since only CO_2 generated in the calciner can be captured. Indirect calcination has been designed such that it is integrated with a heat recovery steam cycle to minimize the energy penalty involved [1]. Even though the reference indirect calcination design was proposed for CO_2 capture from cement plants, its complete integration has not been analyzed to date. The raw mill, preheater and kiln existing in a conventional cement plant were not included in the process scheme. Furthermore, only the calcination reaction was considered while clay decomposition and clinkerization reactions were not taken into account. Therefore, a complete process integration of this process into a cement plant, aiming to use of the excess energy from high temperature gas streams for cement raw meal preheating has been analyzed in this study. Importantly, a new hybrid carbon capture system has been proposed where an indirect calcination unit captures part of the CO_2 relating to $CaCO_3$ calcination and an aqueous amine process removes the remaining CO_2 relating to clinkerization occurring at cement kiln and fuel combustion for the indirect calcination.

2. Process Descriptions

2.1. Reference Cement Plant

The details of reference dry-feed cement plant including all the major units: raw mill, preheaters, pre-calciner, kiln and clinker cooler were already described in the previous study [6]. To have proper mass and energy balances, all chemical reactions occurring in the process, which can be classified as decomposition and clinkerization reactions were included. The main modeling assumptions and outcomes for the reference cement plant are summarized in Table 1. In the reference plant, the pre-calciner and kiln operate at 915°C and 1450°C, respectively while 10% excess air is considered to guarantee complete combustion in both reactors. For a given raw meal specifications, clinker composition that comprises of alite, belite, tricalcium aluminate and tetracalcium aluminate phases was estimated by the support of reference clinker phase diagram [7]. The simulated clinker composition was in an agreement with that obtained by the Bogue equation [8]. According to the given raw meal and clinker compositions, 1.66 kg/s raw meal is required to produce 1 kg/s clinker. The required thermal energy was estimated to be 3.13 MJ_{th}/kg clinker.

Table 1. Main modeling assumptions for the reference cement plant [6]. (LHV: Lower heating value)

Description		Unit
Raw meal flow rate	52.4	kg/s
Raw meal composition	72.5% Calcite, 5.0% Quartz, 9.0% Pyrophyllitte, 2.4% Kaolinite, 1.8% Goethite, 8.0% Moisture, 0.3% Sulphur	wt%
Clinker production capacity	31.6	kg/s
Clinker composition	60.4% Alite, 17.2% Belite, 10.9 % Tricalcium Aluminate, 8.2 % Tetracalcium Aluminate, 2.5% $CaSO_4$, 0.8% Ash	wt%
Pre-calciner operating temperature	915.0	°C
Kiln operating temperature	1450.0	°C
Fuel in the calciner (LHV)	Coal (26.6)	MJ_{th}/kg
Fuel in the kiln (LHV)	Pet coke (32.8)	MJ_{th}/kg
Excess air ratio	10.0	%
Thermal energy consumption	3.13	MJ_{th}/kg clinker
CO_2 generation intensity	0.81	kg CO_2/kg clinker

2.2. Fundamentals of the Indirect Calcination Process

Figure 1 shows the schematic diagram of a novel indirect calcination process which separates fuel combustion and limestone calcination into two distinct chambers [1]. The calciner operates at 930ºC for the complete calcination of limestone in the raw meal. The high temperature solid stream from the combustor (>1000ºC) is transferred to the calciner to meet heat requirement for the endothermic calcination reaction. The combustor temperature is initially set to 1050°C but altered later to illustrate the effect of temperature difference on solid flux and solid circulation rate. The temperature of combustor should not exceed the commercial limits of existing circulating fluidized bed (CFB) combustion systems. High temperature CFB combustion systems are well established technologies for ore roasting, phyrohydrosis of spent potlining and aluminium hydroxide calcination processes with operating temperatures of 1050ºC, 1200ºC and even up to 1450ºC, respectively [9]. The high operating temperatures in the CFB combustor restrict the fuel characteristics due to ash softening problems. Therefore, the pet coke used in the kiln of the reference cement plant is burnt in the combustor with excess air of 10%, for which the composition is (wt %): 85.6% C, 3.5% H, 1.8% N, 5.3% S, 1.8% O, 0.2% ash and 1.8% moisture [10].

2.3. Process Integration of the Indirect Calcination Process into the Reference Cement Plant

To prevent circulation of significant amount of clay minerals with CaO and their interaction at the given temperature range, limestone and clay minerals are fed into two separate raw mills as presented in Figure 2. The moisture-free limestone from the raw mill is fed to a preheater, where its temperature subsequently increases by heat exchange with hot gas streams from the combustor and cooler. The excess air from the cooler is initially at 279°C but is further heated up to 880°C in a regenerative heat exchanger while the CO_2-rich gas stream leaving the calciner at 930°C is cooled to 330°C. While the limestone stream from the preheater is sent to the calciner solely, the product CaO from this reactor is mixed with preheated clay before the kiln stage.

Since high solid temperatures are achieved in the limestone preheater, it is assumed that 10% limestone in the feed is calcined in the preheater stage [7]. Accordingly the corresponding CO_2 emissions cannot be captured. Having been cooled to certain temperatures in the limestone preheater, the exit gas stream is able to cover the heat requirement in the limestone raw mill and fuel drying unit. Since there is no combustion occurring in the calciner anymore, the tertiary air stream (908°C) can entirely be fed to the combustor. The heat requirement in the kiln reduces with the assumption of complete calcination in the calciner because the calcination efficiency is only 90% in the calciner of the reference cement plant [7]. All surplus secondary air at 1025°C, which is not needed in the kiln anymore, can also be transferred to the combustor. Finally, the excess air from the clinker cooler is able to cover the remaining requirement in the combustor. In the clay preheater, the flue gases from the kiln heats up the clay and leaves the system at 110°C.

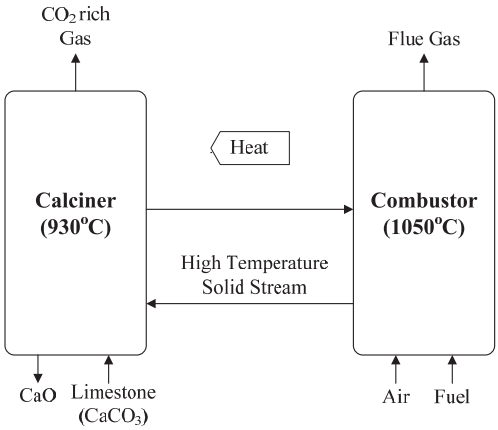

Fig. 1. Schematic diagram of the indirect calcination process [1].

The presence of CaO and SiO_2 in a single preheater system leads to formation of belite phase under the conditions of final preheater stage and pre-calciner [7]. Since the CaO and clay minerals are mixed just before the kiln stage in this configuration, belite formation is postponed. Thus, it would be needed to adjust the residence time in the kiln by controlling its rotational speed so that the same clinker composition with the reference cement plant can be obtained. Accordingly an additional reaction step prior to the kiln stage was included in the simulation of the indirect calcination process where belite formation occurs.

Although air leakages in the raw mills, preheaters and kiln are not so critical for this configuration and included in its simulation, it is very important to minimize air leakage into the calciner to prevent the dilution of the CO_2 rich stream. Also, part of the CO_2 released in the calciner can be transferred to the combustor (or vice versa) on the pores and interparticle voids of the circulated solids even though very low gas transfer rates are expected. Although it is neglected in this study, the negative impacts of air leakages on CO_2 purity should be investigated in further studies.

2.4. Amine Process and its Implementation

To obtain accurate performance predictions for the absorber and stripper in the amine process, the add-on amine thermodynamic package in UniSim Design is employed. The optimization of absorber and stripper design in terms of adjusting the feed gas temperature and pressure has not been examined, and the process conditions given in Ahn et al. [11] have been adapted. The technical modelling parameters for this system are given in Table 2. The level of NO_x and SO_x concentrations in the feed gas stream is crucial for the amine process. These components react with amine to produce amine salts which cannot be dissociated in the stripper. The spent solvent needs to be replaced with fresh solvent which increases the variable cost. Therefore, a flue gas desulphurization (FGD) unit and a selective catalytic reduction (SCR) unit need to also be included in the process scheme for the reduction of SO_x and NO_x emissions. The flue gas stream from the FGD unit is initially sent to a cooler, where it is cooled to 32°C and part of the water in this stream is condensed out. It is then pressurized to 1.31 bar by a blower prior to the absorption stage. The lean amine concentration is set to 30 wt% by adjusting MEA and water make-up flowrates. The CO_2-rich sorbent is pumped to the section at the bottom of the striper that operates at 1.93 bar. A water wash tower is included for the recovery of vaporised MEA which is then sent back to the absorber.

An important design issue for the amine scrubbing process is to satisfy heat duty in the steam stripper for solvent regeneration. The CHP plant configuration detailed in the IEA report [10] is attached into the amine plant, where the main steam at 500°C and 130 bar is blown into a turbine for power generation and is then fed to the reboiler at 144.7°C and 3.5 bar. The power generation in the CHP plant partially/completely fulfils power requirements in both reference cement and carbon capture plants.

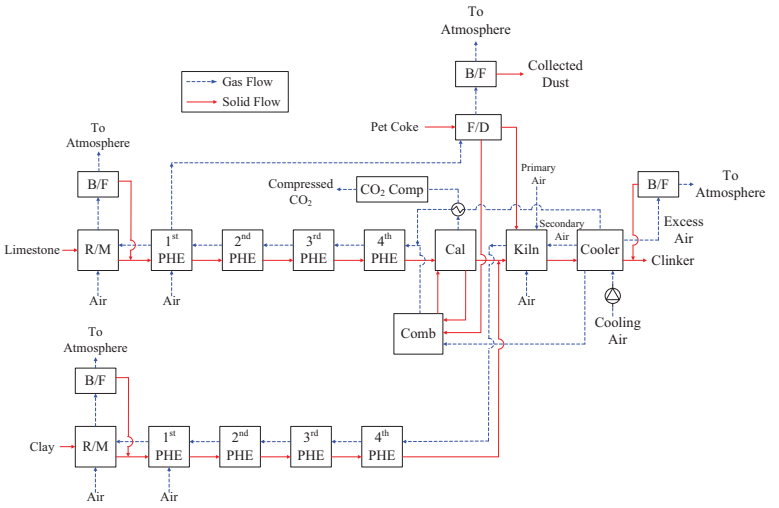

Fig. 2. Schematic diagram of the reference cement plant with the indirect calcination process. Abbreviations: **R/M**, Raw Mill; **B/F**, Bag Filter; **F/D**, Fuel Drying; **PHE**, Preheater; **Cal**, CFB Calciner; **Comb**, CFB Combustor; **CO_2 Comp**, CO_2 Compression.

Table 2. Main modeling parameters for the amine process [11].

Description		Unit
Solvent	Monoethanolamine (MEA)	-
MEA concentration	30	wt%
Absorber feed gas temperature	43.5	°C
Absorber feed gas pressure	1.31	bar
Stripper bottom pressure	1.93	bar
Stripper feed temperature	100	°C
Steam source	CHP plant	-
CHP plant steam condition	500 / 130	°C/bar
Steam provided to the reboiler	144.7 / 3.5	°C/bar
Steam after the reboiler	138.5 / 3.5	°C/bar
NO_x control	Ammonia SCR	-
SO_x control	Wet-limestone FGD	-

Two different configurations have been assessed for the integration of the amine process into the reference cement plant. The corresponding schematic diagrams shown in Figures 3a and 3b are for the hybrid system and the standalone amine process [10], respectively. In the hybrid system, the excess air from the cooler, after being heated up by hot CO_2-rich gas from the calciner, is fed to the CHP plant instead of the limestone preheater. In that way the temperature of solid stream in the limestone preheater and relevant partial calcination level can be kept similar to those in the reference cement plant. The CHP plant with CFB technology simultaneously generates steam for the solvent regeneration and produces electricity. Therefore, the thermal heat requirement in the CFB combustor located in the hybrid system is expected to be higher compared to that of the standalone application of the indirect calcination process. The CHP plant configuration employed in this system would be similar to large scale CFB combustion systems for CHP plants, which are commercially in operation and will be scaled up to 600 MW_e in a near future [12]. The conventional CHP plant layout detailed in [10] has been modified in hybrid system to include solid circulation between the reactors while the reference steam conditions have retained. For the reduction of NO_x emissions, two SCR units are located between the raw mills and the preheaters as suggested in the IEA report [10]. The temperature of gas streams at these locations is around 320°C, and the reductant is selected to be 25% ammonia solution. The flue gases leaving the bag filters are blown into an FGD for SO_x removal. The solvent flow rate in the amine process is varied in order to achieve 90% CO_2 avoidance.

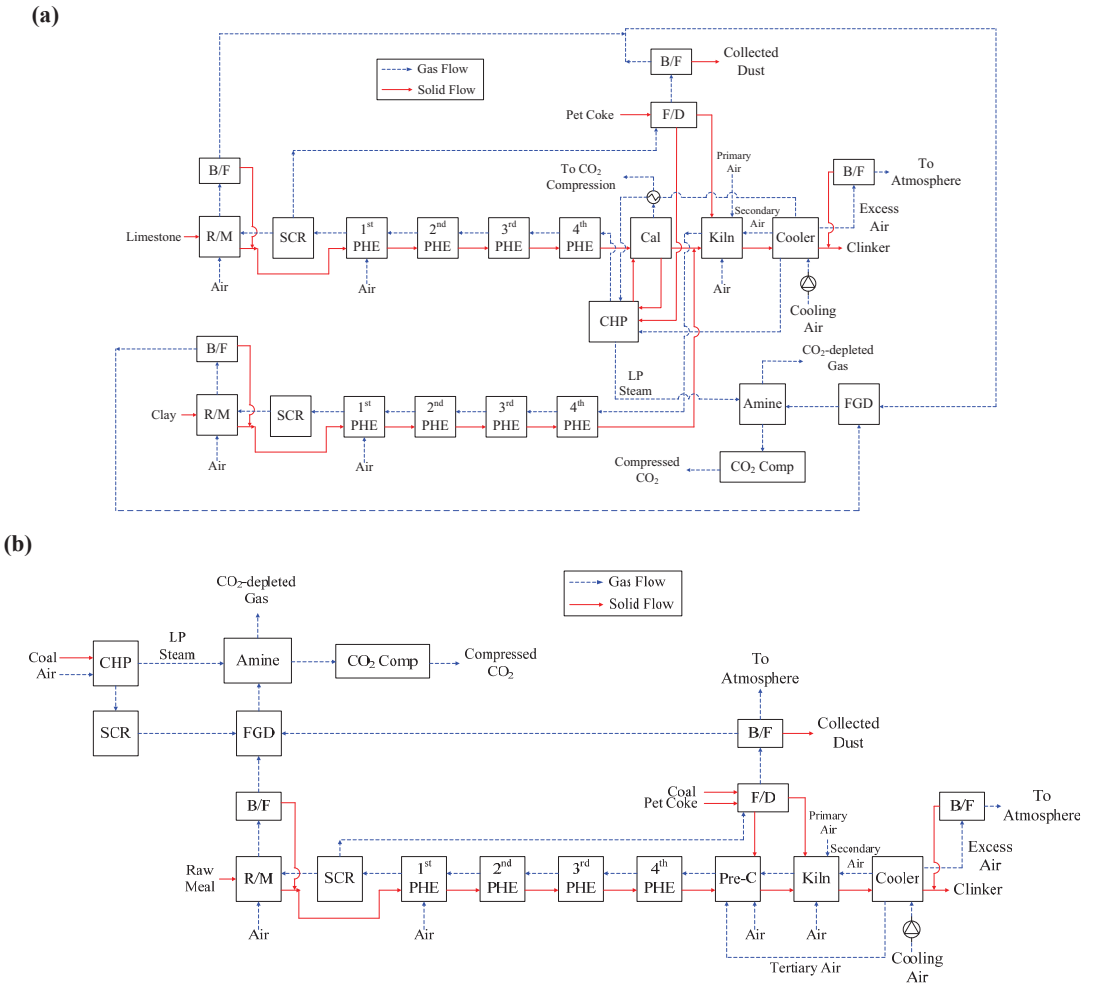

Fig. 3. Schematic diagram of the reference cement plant with the (a) hybrid system; (b) standalone amine process [10]. Abbreviations: **R/M**, Raw Mill; **B/F**, Bag Filter; **F/D**, Fuel Drying; **PHE**, Preheater; **Pre-C**, Pre-calciner; **Cal**, CFB Calciner; **CHP**, Combined heat and power plant; **SCR**, Selective Catalytic Reduction Unit; **FGD**, Flue Gas Desulphurization Unit; **Amine**, Amine Process; **CO_2 Comp**, CO_2 Compression.

The second option presented in Figure 3b shows an end-of-pipe integration of the amine process in the reference cement plant [10]. The same type of coal as in the reference cement plant is burnt in the CHP plant, the composition of which is given as (wt%) 64.4% C, 4.5% H, 1.4% N, 0.9% S, 7.2% O, 12.1% ash and 9.5% moisture [10]. The flue gases from the CHP plant, after passing through an SCR unit, are mixed with the cement flue gases and fed to an FGD unit. The SO_x- and NO_x-depleted flue gases are then transferred to the amine plant. As before, the CO_2 avoidance rate is set to 90% by adjusting the solvent flowrate in the absorber. In all configurations, the CO_2-rich gas stream from the stripper is sent to the CO_2 compression unit, which consists of a four stage compression with intermediate cooling, followed by a pump when the CO_2 becomes a dense phase. The final CO_2 product is compressed up to 150 bar, and adiabatic efficiency of each compressor is assumed to be 75% while the inlet gas temperature of each step is set to 45°C.

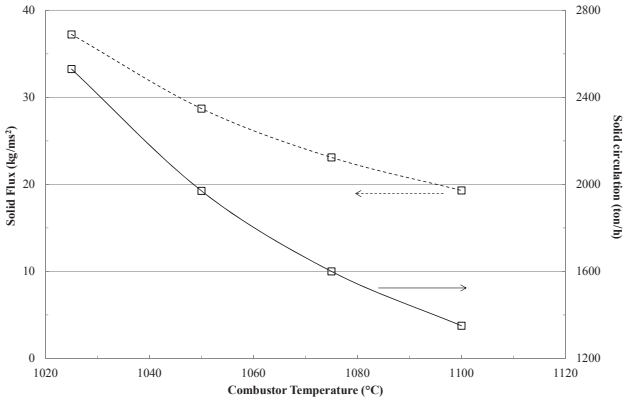

Fig. 4. Variation of solid flux and solid circulation rate in the combustor at different temperatures.

3. Results

The temperature of $CaO/CaCO_3$ stream entering the calciner in the indirect calcination process presented in Figure 2 is 725°C as a result of heat exchange with the hot flue gases in the limestone preheater. The high solid feed temperatures reduce the thermal energy requirement in the calciner so that it is lower compared to that of the reference indirect calcination configuration [1] where almost the same quantity of limestone is fed to the calciner at the ambient temperature. Accordingly the flow rate of the solid recycle is reduced to 1970 ton/h compared to 3200 ton/h reported in the literature. The recycled solid stream comprises of mainly CaO (97 wt%) with some ash and $CaSO_4$.

The temperature of the combustor that is initially fixed at 1050°C in the indirect calcination process is then altered in a range of 1025 - 1100°C to indicate its impact on solid flux and solid circulation rate. The results are presented in Figure 4. The maximum combustor temperature is limited to 1100°C to prevent the increase in the solid temperature and excessive partial calcination rates in the limestone preheater. To estimate the solid flux, the superficial velocity of gases in the reactor was assumed to be 5 m/s being a typical value for CFB systems in fast fluidization regime. The solid recycle rate reaches the minimum at 1100°C with a value of 1350 ton/h. The solid flux estimates in the combustor ranges between 19–37 kg/ms^2 at different combustor temperatures and can be handled by the current status of CFB combustors according to Bi and Liu [13].

The process performances of the proposed carbon capture options are presented in Table 3. In addition, those for the Ca-looping process [6] and Ca-Cu looping process where the Ca-looping process is coupled with a chemical looping combustion (CLC) cycle to eliminate the requirement of energy intensive air separation unit (ASU) [14] have been included for a comparison. The total energy requirement in the standalone indirect calcination process is slightly lower than that of the reference cement plant (98.8 MW_{th}) which can be linked to higher level of heat recovery from the excess air. The main energy penalty for this system results from the CO_2 compression unit. It provides up to ~56% CO_2 avoidance rate without a need of any additional carbon capture technology. By incorporating the amine process into the indirect calcination process, 90% CO_2 avoidance can be achieved. Although the thermal energy requirement of the cement plant in the hybrid configuration seems to be much lower than the other options, it is because of the pre-calciner duty that is included in the heat requirement of the CHP plant.

Table 3. Comparison of standalone indirect calcination and amine processes, hybrid system, and Ca-looping and combined-looping processes in terms of process efficiencies.

	Indirect Calcination	Amine process	Hybrid System	Ca-looping Process [6]	Ca-Cu Loop. Process [14]
Thermal energy requirement					
in the cement plant (MW_{th})	96.8	99.0	24.0	48.9	85.0
in the capture plant (MW_{th})	-	243.3	136.6	132.3	139.3
Total (MW_{th})	96.8	342.3	160.6	181.2	224.3
Amine process					
Feed gas composition (mole %)	-	2% H_2O, 4% O_2, 74% N_2, 20% CO_2	2% H_2O, 7% O_2, 77% N_2, 14% CO_2	-	-
CO_2 in feed (kgmole/h)	-	3891.2	1425.0	-	-
CO_2 capture efficiency (%)	-	95	85	-	-
CO_2 lean loading (mole/mole)	-	0.233	0.233	-	-
CO_2 rich loading (mole/mole)	-	0.46	0.51	-	-
Solvent regeneration energy requirement (MJ_{th}/kg CO_2)	-	3.96	3.28	-	-
Power consumption					
Cement plant auxiliaries (MW_e)	13.7	13.7	13.7	13.7	13.7
Capture plant					
CO_2 compression (MW_e)	5.7	15.0	11.7	13.6	13.1
Plant auxiliaries (MW_e)	1.5	14.3	8.0	2.6	3.1
ASU (MW_e)	-	-	-	9.7	-
Power generation (MW_e)	-	50.2	13.6	37.6	53.8
Net power (MW_e)	–20.9	7.2	–19.8	-2.0	23.9
CO_2 intensity (kg CO_2/kg clinker)	0.36	0.08	0.08	0.08	0.08
CO_2 avoidance rate (%)	55.6	90.0	90.0	90.0	90.0
Incremental energy consumption (GJ_{th}/ton CO_2 avoided)	1.0	8.1	3.2	2.5	1.7

In the hybrid configuration, the concentration of the CO_2 in the feed gas entering the absorber is around 14 mole% which is a typical value for a coal-fired combustor whereas this value is around 20 mole% for the standalone application of the amine process. The difference is due to the additional CO_2 emissions resulting from the calcination of limestone. Besides, the molar flow rate of the feed gas is less in the hybrid configuration. In order to reach the avoidance rate of 90%, the CO_2 capture efficiency is set to 85% in the hybrid configuration, while up to 95% capture efficiency is required in the standalone amine process because of the excessive CO_2 generation in the CHP plant. For this reason, the duty of reboiler increases to 3.96 MJ_{th}/kg CO_2 in the latter.

The power requirement of the capture plant in the hybrid system is calculated to be 33.4 MW_e. This requirement arises from the cement plant auxiliaries (13.7 MW_e), CO_2 compression unit (11.7 MW_e), pumps and compressors in the amine process as well as FGD and SCR units. The total electricity requirement of 43.0 MW_e in the standalone amine process can be met by the CHP plant where an extra 7.2 MW_e can be potentially exported or sold to the grid. Nevertheless, the gross output of the CHP plant is not enough to meet the entire requirement in the hybrid system so remaining 19.8 MW_e should be imported. The incremental energy consumption goes up to 8.1 GJ_{th}/ton CO_2 in the standalone amine process and is calculated to be 3.2 GJ_{th}/ton CO_2 for the hybrid system at the same avoidance rate. However, it can be observed that alternative CO_2 capture options, the Ca-looping and the Ca-Cu looping processes, require less energy consumption as a result of possible recovery of the heat spent for sorbent regeneration at high temperatures in terms of power generation and the utilization of their purge stream that mainly contains CaO for cement manufacture, lowering the thermal energy consumption in the cement plant.

4. Economic Analysis

It is important to take economic criteria into account for the comparison of different carbon capture technologies. A simple and transparent economic analysis has been given for the estimation of costs of cement production and CO_2 avoided associated with the capture technologies, which was based on the approach given in [10]. Levelised cost of cement (LCOC) that refers the ratio of the net present value of total capital requirement, O&M and variable

costs of a cement plant to the net present value of cement production over its operating life has been calculated. The formulation of the LCOC is given by the following equation:

$$LCOC = \frac{\sum_{t=1}^{n} \frac{TCR_t + M_t + V_t + (TCR_{t,cc} + M_{t,cc} + V_{t,cc})}{(1+r)^t}}{\sum_{t=1}^{n} \frac{C_t}{(1+r)^t}} \quad (1)$$

where TCR_t is the total capital requirement, M_t is the O&M cost, V_t is the variable cost and C_t denotes the cement production rate. The suffix cc refers to carbon capture, and t and r are operating year and discount rate, respectively. By knowing the difference between the LCOC estimations for the reference cement plant and a capture case, and the CO_2 emissions for each case, the cost of CO_2 avoided can be calculated according to the following equation:

$$Cost\ of\ CO_2\ avoided = \frac{LCOC_{cc} - LCOC_{base}}{[ton\ CO_2/ton\ cement]_{base} - [ton\ CO_2/ton\ cement]_{CC}} \quad (2)$$

The main financial assumptions were taken from the IEA report [10] and IEA GHG R&D programme Technical & Financial Assessment Criteria [15]. The 'S' curve of expenditure is selected as 20%, 45% and 35% of TCR for the first three years, respectively. An operating life of twenty five years with a construction period of 3 years is assumed. The load factor (or capacity factor) is fixed at 60% on the first year and 90% on the subsequent years. The discount rate of 10% is chosen to express discounted cash flow. The cost results are expressed in Euro (€), and an exchange rate of 1 $=0.7739 € is applied where necessary. In the economic analysis, the main issue is the estimation of TCR of each system. The routine and breakdown maintenance is allowed for at 3.5% per year of the TCR for the plants handling solids and at 1.7% per year for the plants handling gases and liquids according to the IEA report [10]. An escalation factor of 1.5% is included for the estimation of O&M cost during the operating life. The operating labour is assumed to work in a 5 shift pattern with an annual salary of €40000/yr. An allowance of 20% of the operating cost is added to cover supervision and an additional 30% for administration and general overheads.

The reference cement plant capital cost allocation has been reported in [10], and the calculations and assumptions were replicated here for the reference cement plant. The reference capital cost and variable cost data for the capture processes reported in Table 4 were obtained from the relevant references [10, 16, 17]. The reference variable cost data has been updated by using 1.5% escalation factor per year to estimate current prices. The electricity cost was set to 0.05 €/kWh. This same electricity cost was utilized as revenue for on-site power generation. An average annual escalation factor of 1.5% was considered in all variable cost calculations for the subsequent years.

The main components of the TCR in the standalone indirect calcination process are a CFB combustor and a CO_2 compression unit. Because, the first is similar to the boiler of an air-fired CFB power plant, the TCR estimations given in the DOE report [16] for this plant have been divided into two categories: boiler island and steam cycle. The cost of the CFB combustor in the indirect calcination process can then be calculated based on the total thermal heat requirement in this reactor. For the amine-scrubbing process, the cost structure is designed to include the absorber, desorber, compressors, pumps, heat exchangers and CO_2 compression unit. The reference heat transfer coefficients required sizing the heat exchangers and heat exchanger types in the amine process have been taken from the similar type of work, in addition to the costs of the absorber, desorber and reboiler at known capacity [17]. The costs associated with the heat exchangers, pumps and compressors were calculated by using the CAPCOST software [18]. The absorber and stripper were sized by the Tray Sizing Tool in UniSim based on packed bed column using Flexipac 250Y and IMTP #40, respectively. Since it is not possible to size some auxiliaries in the amine process such as reflux accumulator, filtration and reclaimer by the process simulator, the costs of these units were assumed to be 8% of the TCR of the amine process according to [17]. The cost of a CHP plant including an SCR unit was estimated based on the thermal energy demand of this plant. Even though the costs of the FGD and SCR units which have been included in TCR estimates of all the process schemes presented in this study were estimated based on volumetric gas flow rate, it is worth to mention that more accurate predictions can only be achieved if detailed cost data for such systems are provided. All capital cost estimates were updated by using Marshall & Swift cost index [19] to adjust historic costs to current prices, and the final costs were estimated by employing sixth-tenths rule [20]. To reveal the potential advantage of CO_2 capture, additional benefit of emission trading system (ETS) has been taken into consideration. An additional cost of 14 €/ton CO_2 [21] has been adopted to penalize CO_2 emissions.

Table 4. Reference capital and variable cost data. (*) Based on lower heating value (LHV) of a fuel.

	Capacity	Cost	Reference
Reference cement plant	114.9 ton clinker/h	263.0 M€	IEA [10]
CO_2 compression unit	26.9 MW_e	72.2 M$	DOE [16]
CFB air-fired combustor	1884 GJ_{th}/h*	164 M$	DOE [16]
Absorber (Amine)	1110 m^3	8.3 M$	DOE [17]
Stripper (Amine)	238 m^3	1.9 M$	DOE [17]
Reboiler (Amine)	125 MW_{th}	2.4 M$	DOE [17]
CHP plant	746 GJ_{th}/h*	146.4 M€	IEA [10]
FGD unit	143 m^3/s at 50°C	49.8 M€	IEA [10]
SCR unit	89 m^3/s at 320°C	10.2 M€	IEA [10]
Raw material + Process water	-	6.1 €/ton cement	IEA [10]
Limestone for FGD	-	3.0 €/ton	IEA [10]
Ammonia	-	2000 €/ton	IEA [10]
MEA	-	1100 €/ton	IEA [10]
SCR catalyst	-	1.2 M€/year	IEA [10]
Pet coke	-	80.0 €/ton	IEA [10]
Coal	-	65.0 €/ton	IEA [10]
Electricity	-	0.05 €/kWh	IEA [10]

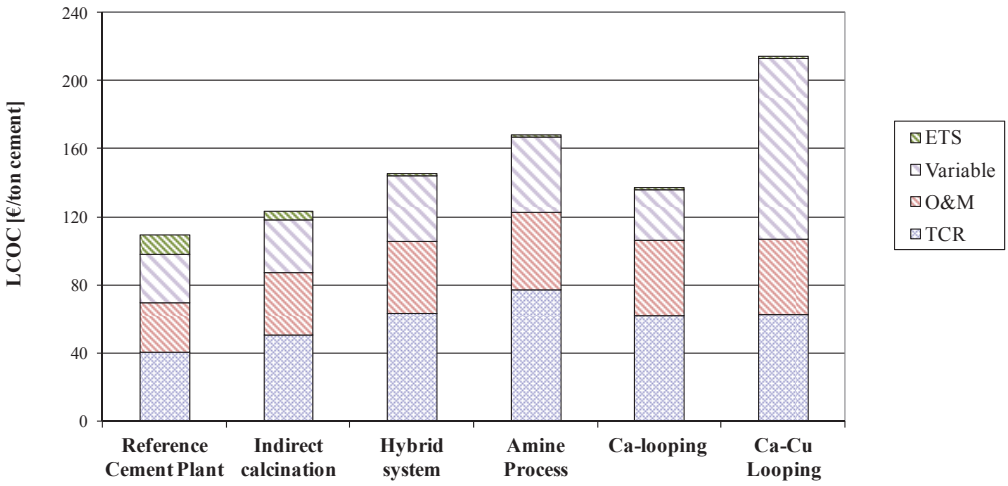

Fig. 5. The LCOC estimates for the reference cement plant, indirect calcination process, hybrid system, standalone amine, Ca-looping [6] and combined-looping processes.

The LCOC estimates for the reference cement plant and different carbon capture options are presented in Figure 5. The LCOC for the standalone indirect calcination process is only 14 €/ton cement higher than that of the reference cement plant. Although the TCR and O&M costs are greater for the indirect calcination process, the total difference reduces with the inclusion of the ETS price. The total TCR of the standalone amine process is significantly higher than that of the reference cement plant, whereas the hybrid system provides around a 15% improvement in the TCR even though both processes provide 90% CO_2 avoidance rate. The LCOC ascends to 145 €/ton cement for the hybrid process and 168 €/ton cement for the standalone amine process. For the latter, the LCOC estimate further increases to 171 €/ton cement for the case where the surplus electricity generation cannot be considered as a revenue. Even though there is no power generation facility in the standalone indirect calcination process, its variable cost estimation is very low due to the absence of excessive costs of fuel and solvent. On the other hand, it is obvious that the Ca-looping process is able to provide the same CO_2 avoidance rate with a lower cost. For the case of Ca-Cu

looping process, the major drawback is the excessive cost of oxygen carrier required for the transfer of oxygen in air. The possible recovery and reuse of part of the oxygen carrier in the purge stream will reduce the variable cost significantly, but this option was not included in the analysis. For the indirect calcination process, the cost is estimated to be around 34 €/ton CO_2 avoided and increases further to 55 €/ton CO_2 avoided in the hybrid system and 89 €/ton CO_2 avoided (95 €/ton CO_2 avoided without surplus power revenue) in the amine process. The utilization of the Ca-looping process reduces the cost down to 42 €/ton CO_2 avoided.

5. Conclusion

It was proven that the indirect calcination process can provide partial CO_2 reduction and energetic efficiency improvement when it is properly integrated into a cement plant. Up to approximately 56% of CO_2 emissions released in the cement plant can be avoided. An amine process was coupled with the indirect calcination process to increase CO_2 avoided efficiency further up to 90%. Among two different process integration options, the incremental energy consumption of the hybrid system is significantly lower than that of the standalone application of the amine process. Furthermore, it provides a more economical solution for the reduction of CO_2 emissions. The cost increases up to 89 €/ton CO_2 avoided when the amine process is retrofitted to the reference cement plant, while it was estimated to be 55 €/ton CO_2 avoided for the hybrid system. The possibility of the use of Ca-looping process in a place of the amine process in the hybrid system would be a promising alternative to reduce the energy consumption and the associated cost.

Acknowledgements

Financial support from the Turkish Ministry of Education and EPSRC (Grants No.: EP/F034520/1, EP/G062129/1, and EP/J018198/1) are gratefully acknowledged.

References

[1] Rodríguez N, Murillo R, Alonso M, Martinez I, Grasa G, Abanades JC. Analysis of a process for capturing the CO_2 resulting for pre-calcination of limestone in a cement plant. Industrial & Engineering Chemistry Research 2011;50 (4): 2126–2132.

[2] Stocker TF, Qin D, Plattner GK, Tignor M, Allen SK, Boschung J, Vasconcellos de Menezes V. Climate Change 2013. The Physical Science Basis. Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change-Abstract for decision-makers. Groupe d'experts intergouvernemental sur l'evolution du climat/Intergovernmental Panel on Climate Change-IPCC 2013, C/O World Meteorological Organization, 7bis Avenue de la Paix, CP 2300 CH-1211 Geneva 2 (Switzerland).

[3] Metz B, Davidson OR, Bosch PR, Dave R, Meyer LA. Summary for Policymakers. In Climate Change 2007:Mitigation; Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change 2007; Cambridge University Press: Cambridge, U.K., New York.

[4] CW Group. Global Cement Volume Forecast Report, 2012.

[5] IEA. World Energy Outlook 2009.U.S. Department of Energy: Washington, DC.

[6] Ozcan DC, Ahn H, Brandani S. Process integration of a Ca-looping carbon capture process in a cement plant. International Journal of Greenhouse Gas Control 2013; 19: 530-540.

[7] Taylor HFW. Cement Chemistry, Academic Press Ltd, New York; 1990.

[8] Bogue RH. Calculation of the Compounds in Portland Cement. Industrial & Engineering Chemistry Analytical Edition 1929; 1 (4): 192-197.

[9] Reh L. New and efficient high-temperature processes with circulating fluid bed reactor. Chemical Engineering & Technology 1995; 18 (2): 75-89.

[10] IEA. CO_2 Capture in the Cement Industry, July 2008/3.

[11] Ahn H, Luberti M, Liu Z, Brandani S. Process configuration studies of the amine capture process for coal-fired power plants. International Journal of Greenhouse Gas Control 2013; 16: 29-40.

[12] Nuortimo K. Large scale CHP with CFB technology. Presented at 4th European Conference of Renewable Heating and Cooling, 2013, Dublin, Ireland.

[13] Bi XT, Liu X. High density and high solid flux CFB risers for steam gasification of solids fuels. Fuel Processing Technology 2012; 91 (8): 915-920.

[14] Ozcan DC, Bocciardo D, Ferrari MC, Ahn H, Kierzkowska AM, Muller CR, Brandani S. Comparison of Various Carbon Capture Technologies to Reduce CO_2 Emissions from a Cement Plant. Presented at AIChE 2013 Annual Meeting, 2013, San Francisco, USA.

[15] IEA GHG. Technical & Financial Assessment Criteria, 2003. Revision B2.

[16] Alstom Power Inc. and National Energy Technology Laboratory, US Department of Energy (DOE). Greenhouse Gas Emissions Control By Oxygen Firing In Circulating Fluidized Bed Boilers: Phase 1 - a Preliminary Systems Evaluation, 2003.

[17] Fisher KS, Beitler C, Rueter C, Searcy K, Rochelle G, Jassim M Integrating MEA Regeneration with CO_2 Compression and Peaking to Reduce CO_2 Capture Costs (No. DOE/ER/84111). Trimeric Corporation, 2005.
[18] Turton R, Bailie RC, Whiting WB, Shaeiwitz JA, Bhattacharyya D, Analysis, Synthesis, and Design of Chemical Processes. 3rd ed. Prentice Hall; 2009.
[19] Marshall & Swift cost index. http://www.marshallswift.com.
[20] Katell S, Welmann P. Process Evaluation Cost Analysis Seminar. Morgantown, WV: U.S. Bureau of Mines 1968: 11-31.
[21] IEA GHG. Biomass CCS Study: Techno-Economic Evaluation of Biomass Fired or Co-Fired Power Plant with Post-Combustion CO_2 Capture, IEAGHG 2009: Cheltenham, U.K.